

Combining high conductivity with complete optical transparency: A band-structure approach

J. E. Medvedeva and A. J. Freeman

Department of Physics and Astronomy, Northwestern, Evanston, Illinois 60208-3112

A comparison of the structural, optical and electronic properties of the recently discovered transparent conducting oxide (TCO), nanoporous $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$, with those of the conventional TCO's (such as Sc-doped CdO) indicates that this material belongs conceptually to a new class of transparent conductors. For this class of materials, we formulate criteria for the successful combination of high electrical conductivity with *complete* transparency in the visible range. Our analysis suggests that this set of requirements can be met for a group of novel materials called electrides.

PACS number(s): 71.20.-b, 72.20.-i, 78.20.Bh

Transparent conducting oxides (TCO) have been known for almost a century¹ and employed technologically for decades. Today, the area of practical applications of this special class of materials which can simultaneously act as a window layer and as an electrically conducting contact layer, is very large²⁻⁴: it includes optoelectronics (invisible circuits), flat-panel displays, energy supply (solar cells) and energy conservation ("smart" windows) devices. The commercial demand for less expensive, more flexible, environmentally friendly materials that exhibit both high optical transmission and electrical conductivity continues to stimulate further research.

All well-known and widely used TCO's (such as In, Sn, Zn, Cd, Ga and Cu oxides and their blends) share similar chemical, structural and electronic properties as well as carrier generation mechanisms. These oxides of post-transition (or transition) metals have relatively close-packed structure with four or six-fold coordinated metal ions. Upon introduction of native or substitutional dopants, they show high transparency in the visible range ($\sim 80\text{-}90\%$) and high electrical conductivity (up to $\sim 10^4$ S/cm). Common to all known TCO's, a highly dispersed band at the bottom of the conduction bands is the most important feature of the host electronic band structure. It provides both (i) the high mobility of the extra carriers (electrons) due to their small effective masses and (ii) low optical absorption due to a pronounced Burstein-Moss shift which helps to keep intense interband transitions out of the visible range⁵.

To illustrate how doping alters the electronic band structure of host transparent conductors, we present the calculated band structure of undoped and Sc-doped CdO , cf., Fig. 1, determined with the full-potential linearized augmented plane wave method⁶ (FLAPW) within the screened-exchange LDA approach⁷. Despite a rather small (indirect) bandgap of ~ 1 eV in pure CdO (as compared to bandgaps of ~ 3.0 eV in undoped In_2O_3 , ZnO and SnO_2), the optical window significantly broadens upon doping (Burstein-Moss shift) so that the intense interband transitions from the valence band are > 3.0 eV (Fig. 1(b)). The high dispersion of the band at the bottom of the conduction band also provides a relatively low intensity of interband transitions from the partially occupied band at the top of the conduction band. Finally,

the small effective masses obtained in pure CdO , $0.25 m_e$, contribute to the observed high carrier mobility in doped CdO (up to $\sim 600 \text{ cm}^2/\text{V s}$, Ref. 8).

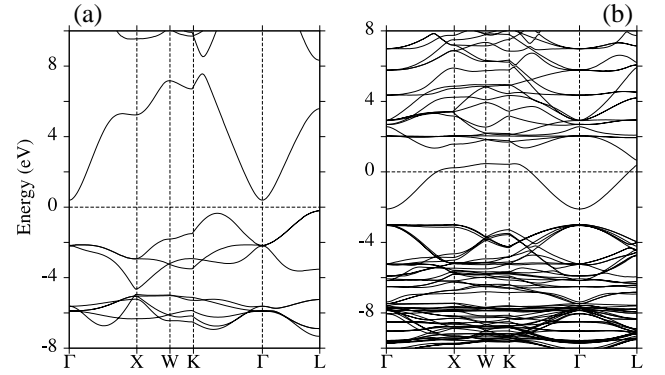


FIG. 1. The electronic band structure of (a) undoped and (b) Sc-doped CdO .

Recently, an insulator-conductor conversion was discovered in an oxide that differs essentially from the known TCO by its chemical and structural properties and by the origin of the induced conductivity: the cage structured insulating calcium-aluminum oxide, $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$, or mayenite, showed a persistent conductivity upon doping with hydrogen followed by ultraviolet irradiation⁹. First-principles electronic band structure calculations¹⁰ have already revealed that the charge transport associated with the electrons excited off the hydrogen ions ($\text{H}^- \rightarrow \text{H}^0 + e^-$) occurs by electron hopping through the encaged "defects" – the H^0 and OH^- located inside the large (more than 5.6 \AA in diameter) structural cavities. The low conductivity of the material (~ 1 S/cm) was attributed to the strong interactions between the UV released electrons which migrate along a narrow conducting channel – the hopping path. Indeed, the alleviation of their electronic repulsion¹¹ resulted in the observed¹² 100-fold enhancement of the conductivity in the mayenite-based oxide, $[\text{Ca}_{12}\text{Al}_{14}\text{O}_{32}]^{2+}(2e^-)$, although the carrier concentration is only two times larger than that in the H-doped UV-irradiated $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$. The improved conductivity, however, came at the cost

of greatly increased absorption^{11,12}, making this oxide unsuitable for practical use as a transparent conducting material.

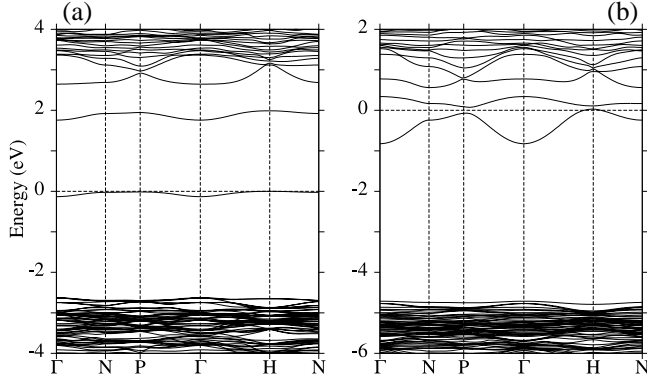


FIG. 2. The electronic band structure of H-doped mayenite (a) before and (b) after UV-irradiation.

Despite the failure to combine effectively the low optical transparency and useful electrical conductivity in the mayenite-based oxides, the nature of their electronic band structure^{10,11} suggests that these materials belong to a conceptually new class of TCO's. As shown in Fig. 2, hydrogen annealing and the subsequent UV-irradiation of $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ results in the formation of a *new* hybrid "defect" band in the band gap of insulating mayenite. This band crosses the Fermi level making the system conducting. Further, the transitions from the occupied part of the band to the unoccupied one are below the visible range due to the narrowness of the hybrid band, while the interband transitions to the bottom of the conduction band are rather weak since they are provided by the low density of states (DOS) in the hybrid band near E_F . Consequently, any increase of the DOS at E_F that favors a higher conductivity, would result in an increase of light absorption, reducing the optical transmission. Indeed, this was observed¹² for $[\text{Ca}_{12}\text{Al}_{14}\text{O}_{32}]^{2+}(2e^-)$, where the DOS at E_F is found to be 24 times larger than in the H-doped UV-irradiated mayenite¹¹.

Thus, in striking contrast to the conventional TCO's, where the optical absorption cannot be eliminated, the band structure analysis of mayenite-based oxides suggests an approach to combine 100% optical transparency and high electrical conductivity. The schematic band structure of such an "ideal" TCO is shown in Fig. 3. The introduction of a *deep* impurity band in the bandgap of an insulating material would help to keep intense interband transitions (from the valence band to the impurity band and from the impurity band to the conduction band) above the visible range. This requires the band gap of a host material to be more than 6.2 eV. Furthermore, the impurity band should be narrow enough (less than 1.8 eV) to keep intraband transitions (as well as the plasma frequency) below the visible range.

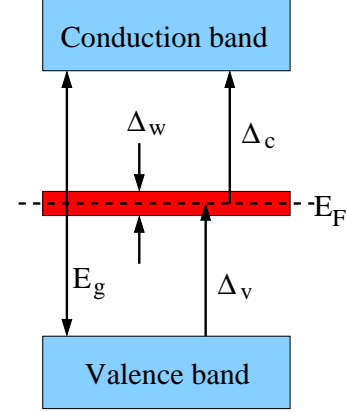


FIG. 3. The schematic band structure of "ideal" TCO: $\Delta_w < 1.8$ eV, $\Delta_v > 3.1$ eV and $\Delta_c > 3.1$ eV provide 100% transparency in the visible range.

To achieve high conductivity, the concentration of impurities should be large enough so that their electronic wavefunctions overlap and form an impurity *band*. The formation of the band would lead to a high carrier mobility due to the extended nature of these states resulting in a relatively low scattering. For this, a material with a close-packed structure should not be used, because large concentration of impurities would result in (i) an increase of ionized impurity scattering which limits electron transport¹³; and (ii) large relaxation of the host material, affecting its electronic structure and, most likely, decreasing the desired optical transparency. Alternatively, nanoporous structure materials offer a way to incorporate a large concentration of impurities without any significant changes in the band structure of the host material, e.g., H^- and OH^- in the spacious cages of mayenite. However, such encaged impurities would be well-separated from each other and, therefore, would not form by themselves an impurity band that is necessary for creating extended well-conducting electronic states¹⁴. The coupling between impurities can be achieved by choosing a material where an array of connected structural cavities (channels) will allow the interaction of the nearby impurities – unlike the mayenite-type materials where the encaged impurities are isolated. For this, novel materials called electrides¹⁵ seem to be very promising candidates for "ideal" TCO's due to their unique structural, optical and electronic properties – namely, intercavity channels¹⁶, large bandgaps, weak binding of the "excess" electrons and near-metal electronic conductivity^{17–20}.

Finally, while the conductivity in the proposed new type of TCO materials may not exceed the maximum value of the conventional TCO's, i.e., $\sim 10^4$ S/cm (due to similar intrinsic limits²¹), their optical transparency can be expected to be as high as 100% in the visible range of wavelength.

Work supported by the DOE (grant N DE-FG02-

88ER45372) and computational resources provided by NERSC.

-
- ¹ F. Streintz, Ann. Phys. (Leipzig) **9**, 854 (1902); K. Badeker, *ibid.* **22**, 749 (1907).
- ² G. Thomas, Nature **389**, 907 (1997).
- ³ D. S. Ginley, and C. Bright (Eds.), Mater. Res. Bull. **25**, 15 (2000), and articles therein.
- ⁴ S. Stoute, Mater. World **11**, 12 (2003).
- ⁵ O. N. Mryasov, and A. J. Freeman, Phys. Rev. B **64**, 233111 (2001).
- ⁶ E. Wimmer, H. Krakauer, M. Weinert, and A. J. Freeman, Phys. Rev. B **24**, 864 (1981).
- ⁷ R. Asahi, W. Mannstadt, and A. J. Freeman, Phys. Rev. B **59**, 7486 (1999).
- ⁸ M. Yan, M. Lane, C. R. Kannewurf, and R. P. H. Chang, Appl. Phys. Lett. **78**, 2342 (2001).
- ⁹ K. Hayashi, S. Matsuishi, T. Kamiya, M. Hirano, and H. Hosono, Nature **419**, 462-465 (2002).
- ¹⁰ J. E. Medvedeva, A. J. Freeman, M. I. Bertoni, and T. O. Mason, cond-mat/0402218, accepted to Phys. Rev. Lett.
- ¹¹ J. E. Medvedeva, and A. J. Freeman, cond-mat/0404187, submitted to Appl. Phys. Lett.
- ¹² S. Matsuishi, Y. Toda, M. Miyakawa, K. Hayashi, T. Kamiya, M. Hirano, I. Tanaka, and H. Hosono, Science **301**, 626 (2003).
- ¹³ H. Brooks, Adv. Electron. Electron Phys. **7**, 85 (1955); R. B. Dingle, Philos. Mag. **46**, 831 (1955).
- ¹⁴ In mayenite, this was successfully overcome by the UV-irradiation which resulted in the formation of the hybrid band. However, the band was formed not only from the states of the encaged impurities but also from the states of atoms belonging to the cage wall (namely, 3d states of Ca atoms which form the bottom of the conduction band). This led to degradation of the optical properties since the hybrid band was effectively shifted towards the conduction band minimum.
- ¹⁵ J. L. Dye, Science **247**, 663 (1990); J. L. Dye, Nature (London) **365**, 10 (1993).
- ¹⁶ The absence of an array of cavities or channels in mayenite is in accord with the finding that $[\text{Ca}_{12}\text{Al}_{14}\text{O}_{32}]^{2+}(2\text{e}^-)$ cannot be classified as an electride¹¹ as originally suggested¹².
- ¹⁷ J. L. Dye, Inorg. Chem. **36**, 3816 (1997).
- ¹⁸ D. J. Singh, H. Krakauer, C. Haas, and W. E. Pickett, Nature **365**, 39 (1993).
- ¹⁹ V. Petkov, S. J. L. Billinge, T. Vogt, A. S. Ichimura, and J. L. Dye, Phys. Rev. Lett. **89**, 075502 (2002).
- ²⁰ Z. Li, J. Yang, J.G. Hou, and Q. Zhu, J. Am. Chem. Soc. **125**, 6050 (2003).
- ²¹ J. R. Bellingham, W. A. Phillips, and C. J. Adkins, J. Mater. Sci. Lett. **11**, 263 (1992); T. J. Coutts, X. Wu, W. P. Mulligan, and J. M. Webb, J. Electron. Mater. **25**, 935 (1996); J. J. Robbins, and C. A. Wolden, Appl. Phys. Lett. **83**, 3933 (2003).